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(54) **Forming dielectric films**

(57) In a process for forming a plasma CVD fluorine-doped SiO_2 dielectric film, gas supplied to a plasma CVD apparatus includes not only SiH_4 gas, O_2 gas, CF_4 gas and Ar gas but also CO_2 gas, and the amount of carbon and the amount of fluorine in the gas are controlled independently of each other, to form a plasma CVD silicon-based SiO_2 dielectric film doped with fluorine in the concentration range of 4.0×10^{21} atoms/cc to 1.0×10^{22} atoms/cc, and carbon in the concentration range of 3.0×10^{19} atoms/cc to 1.0×10^{21} atoms/cc. Thus, the plasma CVD silicon-based SiO_2 dielectric film having a low dielectric constant and a sufficient "resistance to moisture" is obtained.

Fig. 4

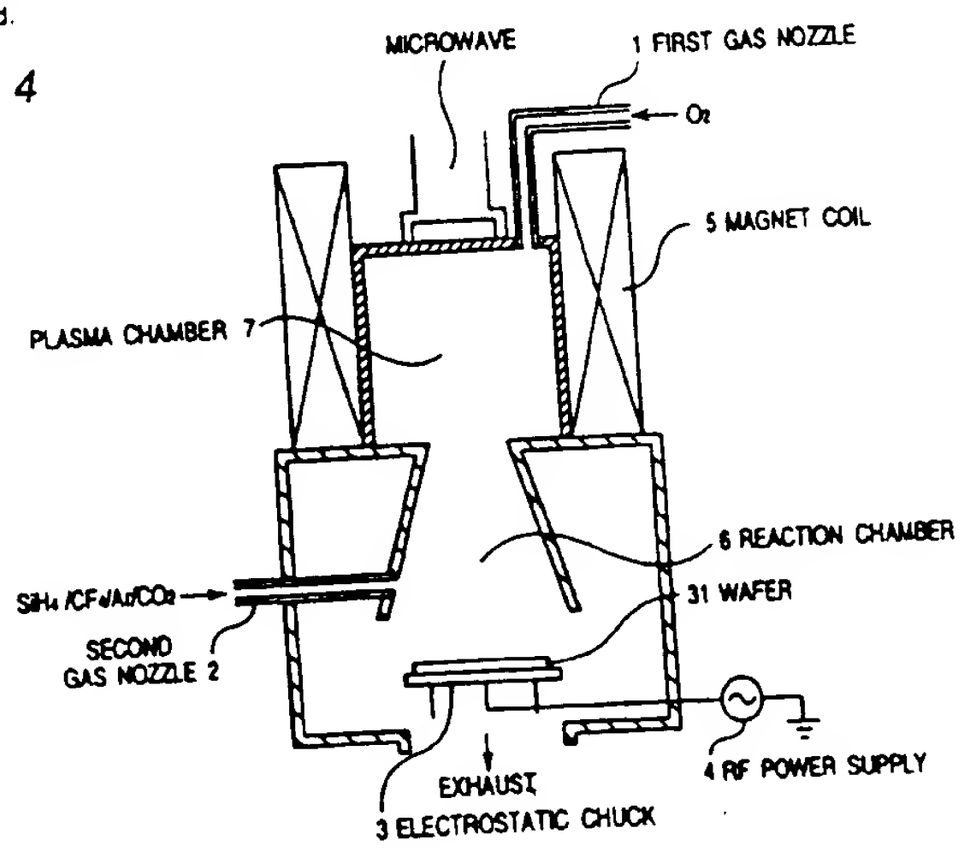

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Fig. 1 PRIOR ART

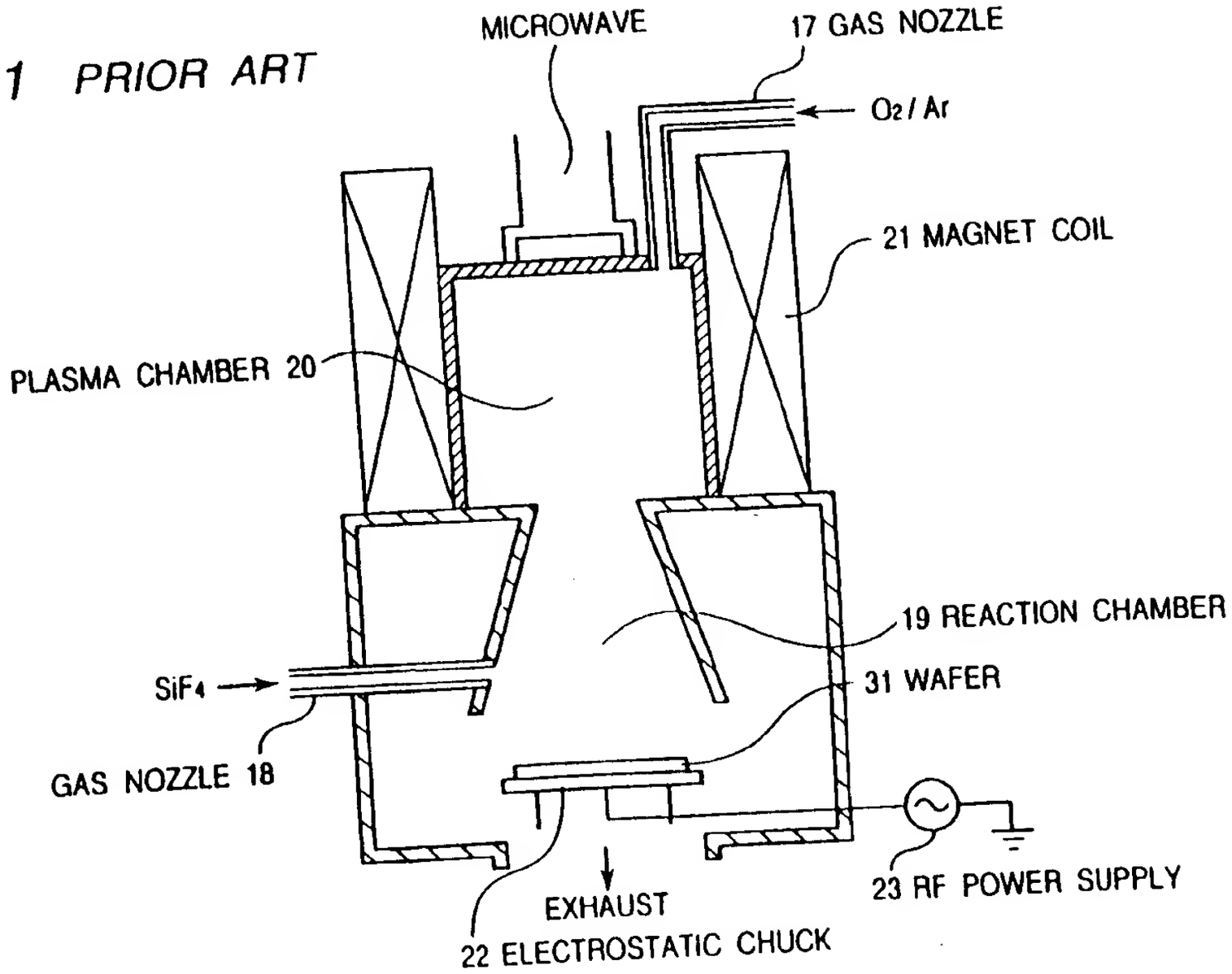


Fig. 2 PRIOR ART

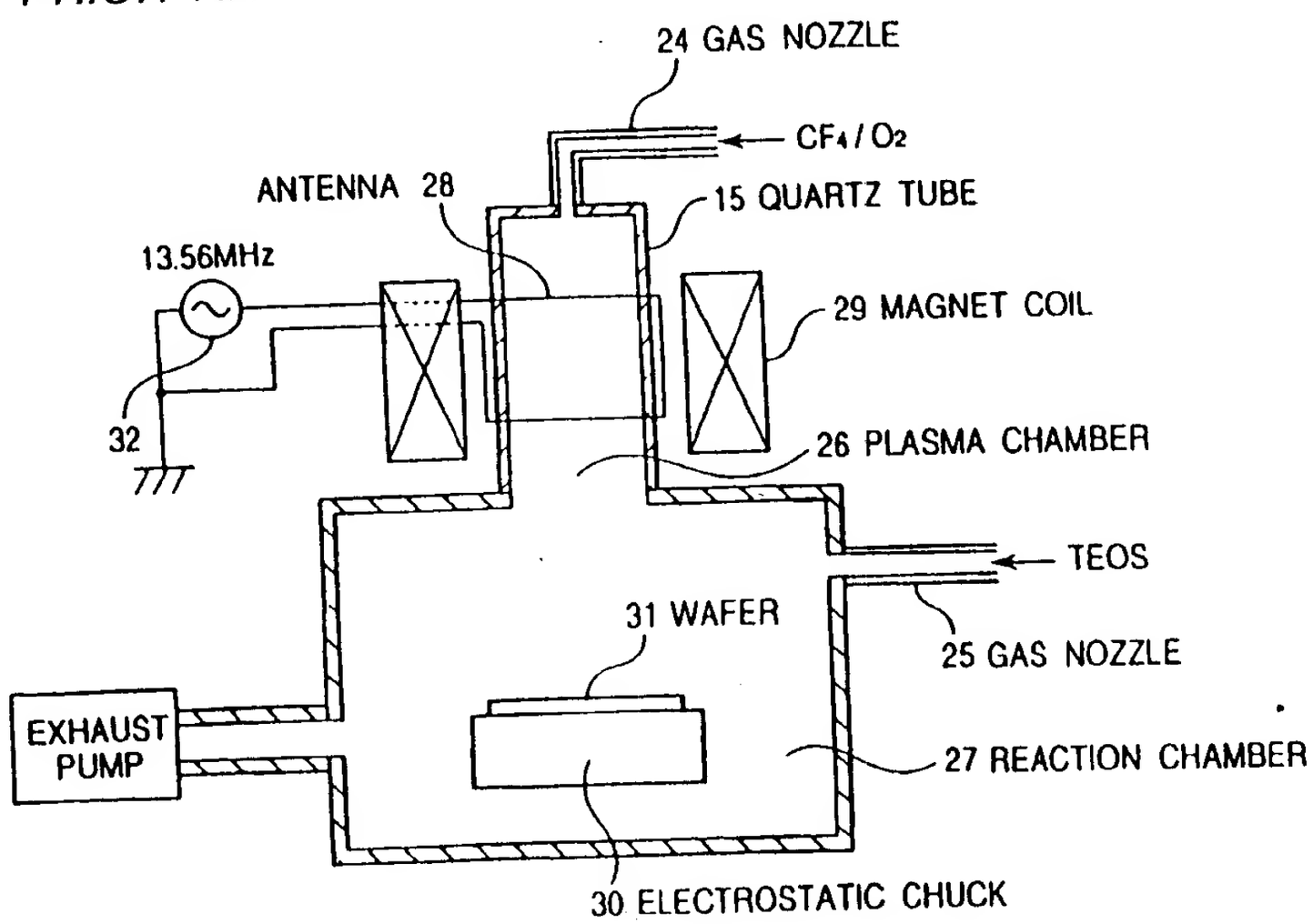


Fig. 3

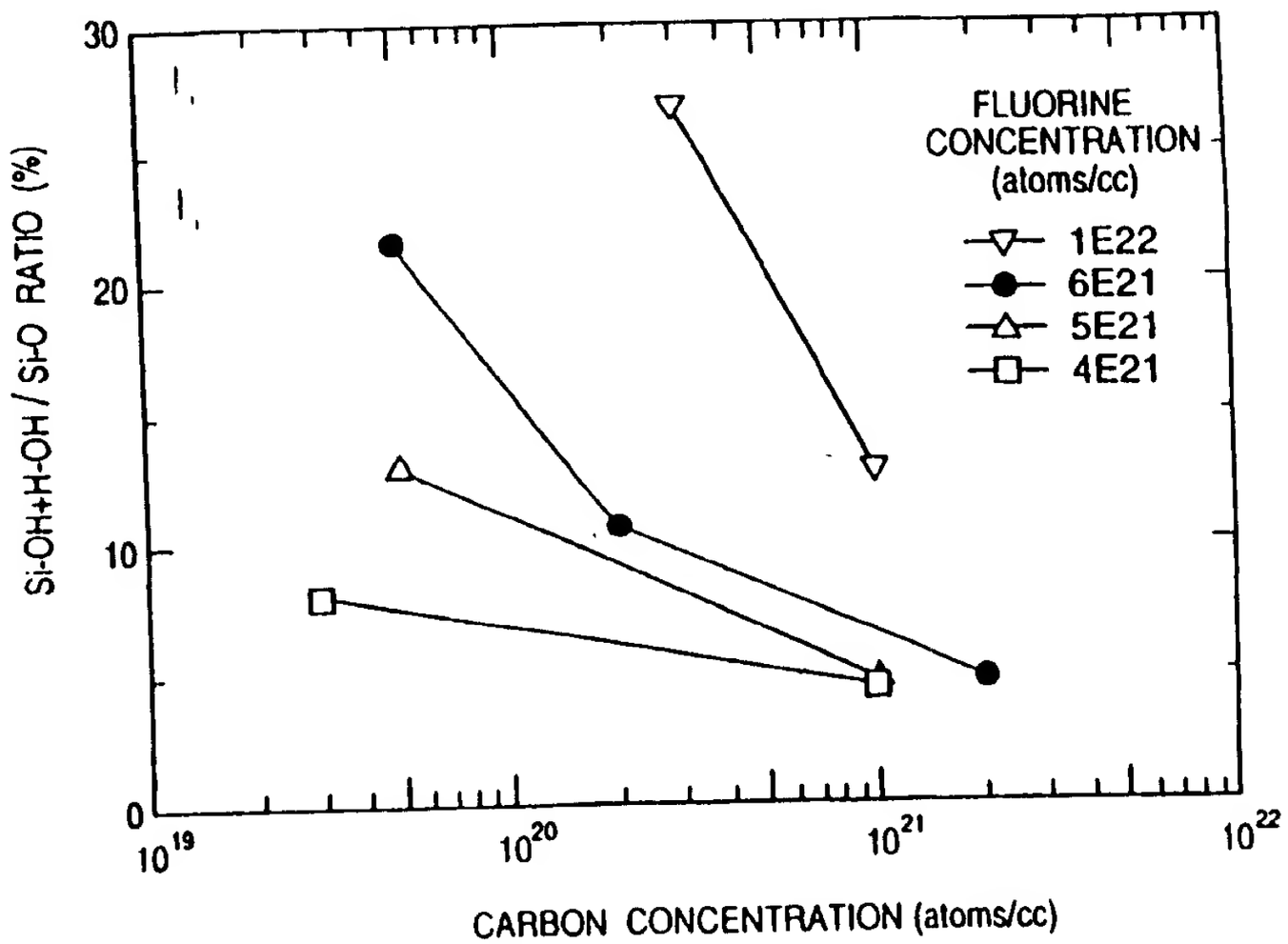

30
20
10
0
Si-OH+H-OH / Si-O RATIO (%)
FLUORINE
CONCENTRATION
(atoms/cc)
1E22
6E21
5E21
4E21
10^{19}
10^{20}
10^{21}
10^{22}
CARBON CONCENTRATION (atoms/cc)

Fig. 4

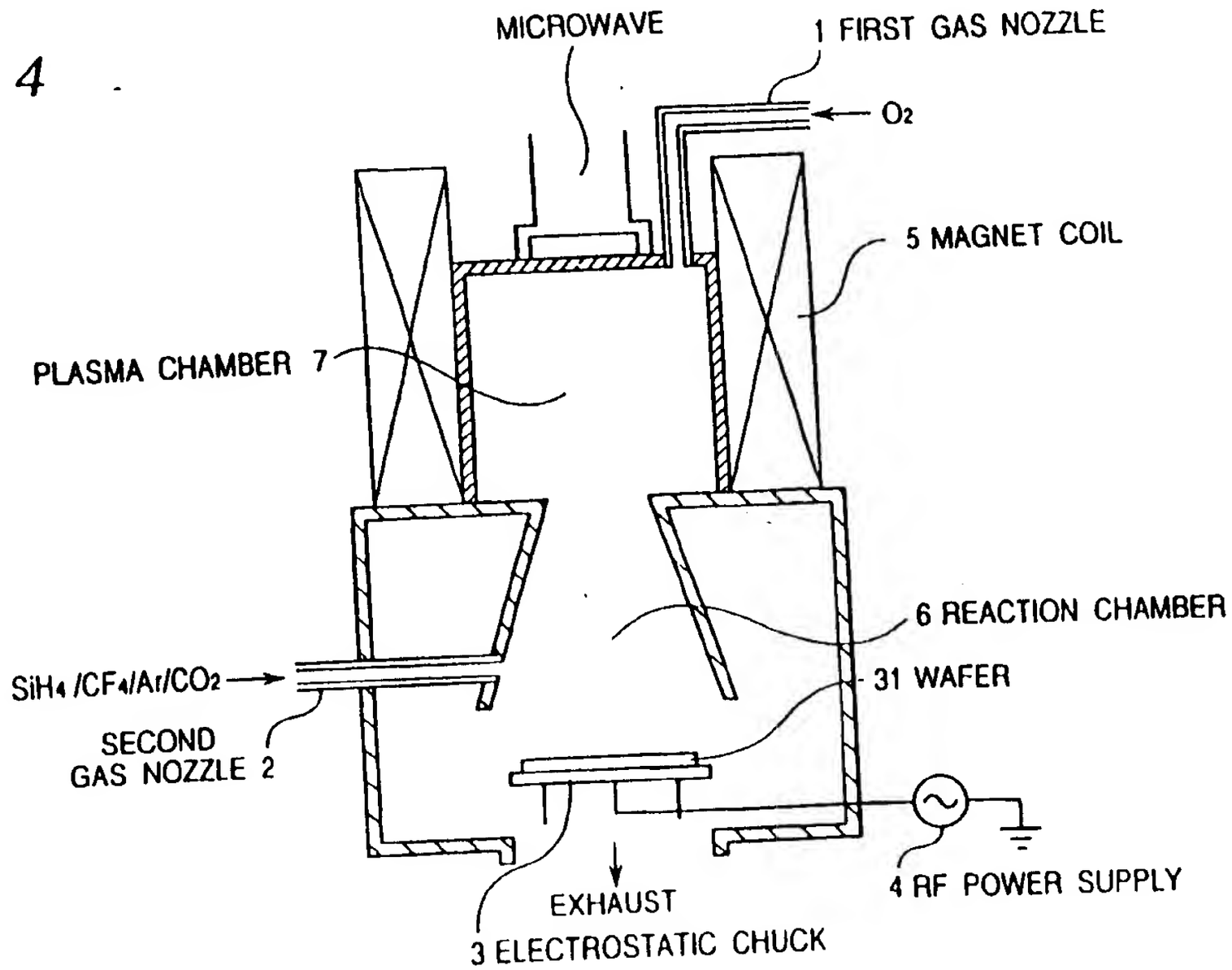
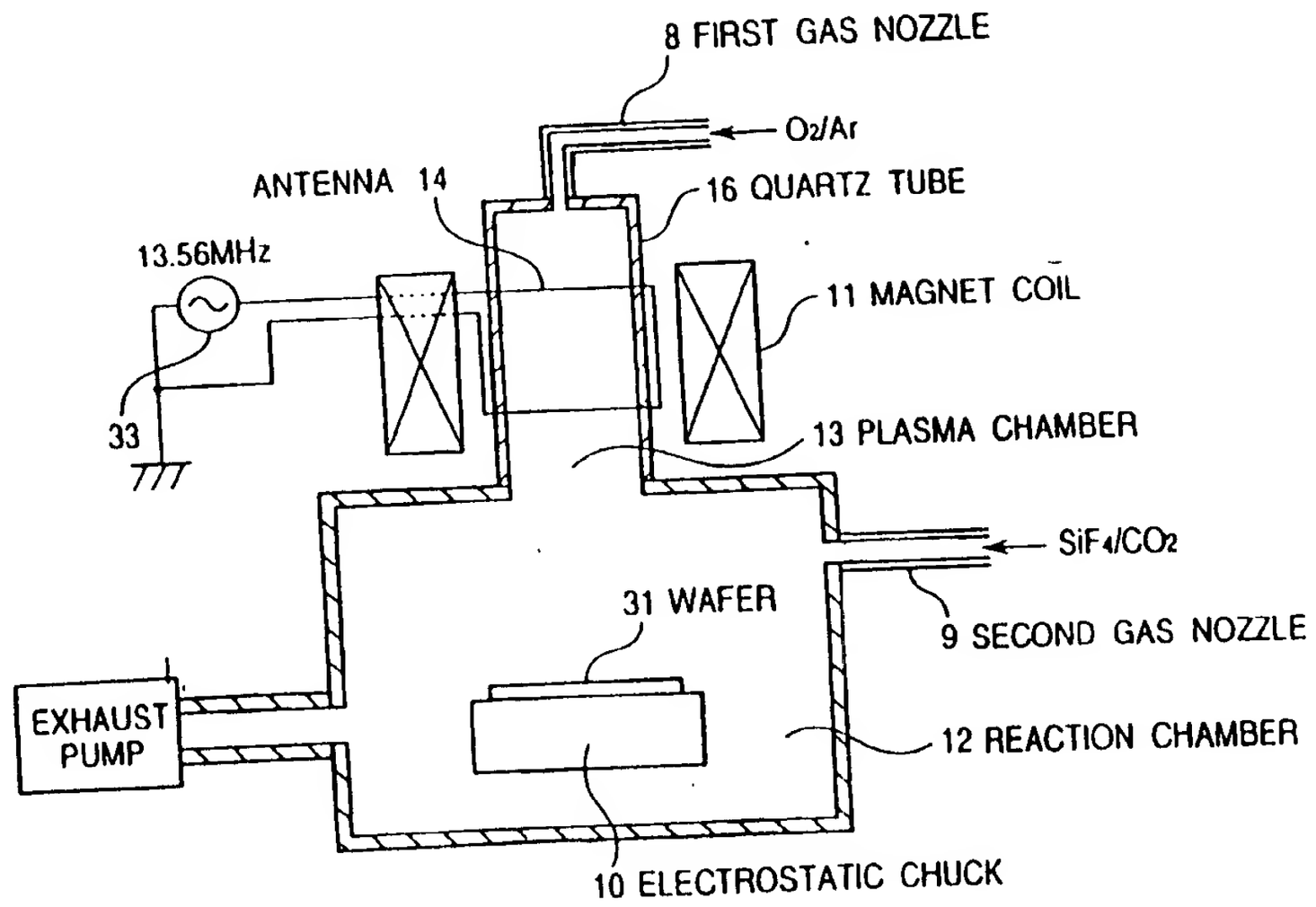

MICROWAVE
1 FIRST GAS NOZZLE
O2
5 MAGNET COIL
PLASMA CHAMBER 7
6 REACTION CHAMBER
SiH4 /CF4/Ar/CO2
31 WAFER
SECOND
GAS NOZZLE 2
EXHAUST
4 RF POWER SUPPLY
3 ELECTROSTATIC CHUCK

Fig. 5


8 FIRST GAS NOZZLE
O2/Ar
ANTENNA 14
16 QUARTZ TUBE
13.56MHz
11 MAGNET COIL
33
13 PLASMA CHAMBER
SiF4/CO2
31 WAFER
9 SECOND GAS NOZZLE
EXHAUST PUMP
12 REACTION CHAMBER
10 ELECTROSTATIC CHUCK

DIELECTRIC FILM AND PROCESS FOR FORMING THE SAME

The present invention relates to a dielectric film, in particular to a plasma CVD dielectric film formed between wiring conductor layers in a semiconductor device, and a method of forming the same.

Description of related art

Recently, a micro-fabrication of a semiconductor integrated circuit has been advanced. In particular, this inclination is remarkable in a multilevel interconnection in a logic integrated circuit. If a spacing between adjacent metal wiring conductors in the multilevel interconnection becomes small, a capacitance between the adjacent metal wiring conductors becomes large, with the result that various disadvantages occur. For example, the speed of an electric signal drops, and a cross talk (giving influence to another signal as a noise) occurs.

One countermeasure is to form an interlayer dielectric film of an insulating material having a low dielectric constant. Recently, there has been reported to lower the specific dielectric constant from the order of 4.5 to the order to 2.8 to 4.3, by changing a plasma silicon oxide film (called a "P-SiO2 film" hereinafter) which was used in the prior art and which was formed in a plasma chemical vapor deposition (called a "P-CVD process" hereinafter), to a fluorine containing plasma silicon oxide film (called a "P-SiOF film" hereinafter).

The dielectric constant can be lowered by increasing the fluorine concentration in the P-SiOF film. However, if the fluorine concentration becomes too large, a "resistance to moisture" (or "resistance to water absorption") is deteriorated. Therefore, at a fluorine concentration which does not deteriorate the "resistance to moisture", the dielectric constant cannot be so lowered (for example, dielectric constant on the order of 3.3). This is reported by N. HAYASAKA et al, "Fluorine Doped SiO_2 for Low Dielectric Constant Films in Sub-Half Micron ULSI Multilevel Interconnection", 1995 International Conference on Solid State Devices and Materials, pages 157-159, the content of which is incorporated by reference in its entirety into this application.

In the case of forming this P-SiOF film in the semiconductor device, planarization is indispensable. In a chemical mechanical polishing (called a "CMP") used for planarizing the P-SiOF film, since a polishing liquid is used, an insufficient "resistance to moisture" becomes a difficult problem. Therefore, when the CMP process is used for planarization, there is no means other than to lower the fluorine concentration thereby to resultantly increase the dielectric constant.

Referring to Fig. 1, there is shown a diagrammatic sectional view of a plasma CVD apparatus for illustrating one example of the process for forming the prior art plasma CVD dielectric film. This example of the prior art process for forming the P-SiOF film (which is one kind of the plasma CVD dielectric film), is described in, for example, T. FUKADA et al, "Preparation of SiOF Films with Low Dielectric Constant by ECR Plasma Chemical Vapor Deposition", 1993 International Conference on Solid State Devices and Materials, pages 158-160, the content of which is incorporated by reference in its entirety into this application.

In order to form this P-SiOF film, first, as material gases, O_2 gas and Ar gas are supplied through a gas nozzle 17 into a plasma chamber 20, and on the other hand, SiF_4 gas is supplied through a gas nozzle 18 into a reaction chamber 19 communicating with the plasma chamber 20. Then, in cooperation of a microwave introduced into the plasma chamber 20 and a magnetic field generated by a magnet coil 21 surrounding the plasma chamber 20, an electron cyclotron resonance (ECR) plasma is created, so that the introduced gases are activated. Thus, a P-SiOF film having an excellent step coverage property is formed on a wafer 31 held on an electrostatic chuck 22 supplied with a RF bias voltage from a RF power supply 23.

The film thus formed is constituted of Si (silicon), F (fluorine) and O (oxygen), and the fluorine concentration is controlled by means of a flow rate of the SiF_4 gas, namely, the SiF_4 gas flow ratio (SiF_4/O_2). However, in the SiF_4 gas, Si and F cannot be controlled independently of each other, and therefore, it is not possible to form the P-SiOF film having a satisfactory low fluorine concentration, and therefore, in an actually formed P-SiOF film, the "resistance to moisture" is not sufficient.

As a countermeasure for the above problem, there has been proposed to add a SiH_4 gas so as to control F independently of Si, thereby to form a P-SiOF film having a relatively low fluorine concentration. This is reported by T. FUKADA et al, "PREPARATION OF SiOF FILMS WITH LOW DIELECTRIC CONSTANT BY ECR PLASMA CVD", 1995 DUMIC Conference, Pages 43-49, the content of which is incorporated by reference in its entirety into this application.

However, in this proposed process, it is considered that not only Si, F and O but also H (hydrogen) are included in a film, so that possibility of formation of Si-OH and H-OH increases, which act as hygroscopic or moisture absorbing sites, with the result that the "resistance to moisture" is deteriorated. In other words, it is very difficult to find out an optimum condition which resultantly gives a satisfactory "resistance to moisture".

Referring to Fig. 2, there is shown a diagrammatic sectional view of a plasma CVD apparatus for illustrating a second example of the process for forming the prior art plasma CVD dielectric film. This second example of the prior art process for forming the P-SiOF film is described in N. HAYASAKA et al, "High-Quality and Low Dielectric Constant SiO_2 CVD Using High Density Plasma", 1993 Dry Process Symposium, pages 162-168, the content of which is incorporated by reference in its entirety into this application.

In this second prior art process, as show in Fig. 2, as material gases, CF_4 gas and O_2 gas are supplied through a gas nozzle 24 into a plasma chamber 26 formed by a quartz tube 15 which is transparent to an electromagnetic wave, and a TEOS (tetraethoxysilane) gas is supplied through a gas nozzle 25 into a reaction chamber 27. In cooperation of a magnet coil 29 surrounding the plasma chamber 26 and an antenna 28 also surrounding the plasma chamber 26 and driven with a 13.56 MHz RF source 32, a helicon plasma is generated and the gas is activated. Thus, a film is formed on a wafer 31 held on an electrostatic chuck 30.

In the above mentioned second prior art process, no RF bias is applied. An example of applying an RF bias is disclosed by R. KATSUMATA et al, "Improvement in Hygroscopicity of PE-CVD F-doped SiO_2", 1995 Dry Process Symposium, pages 269-274, the content

of which is incorporated by reference in its entirety into this application. The film formed in this process is constituted of Si, F, H, C (carbon), and O, but the fluorine concentration is controlled by the flow rate of the CF_4 gas and the ratio of the CF_4 gas to other gases. However, since C and F cannot be controlled independently of each other, the P-SiOF film having a satisfactory "resistance to moisture" cannot be obtained.

In the above mentioned prior art dielectric films and the prior art processes for forming the same, because Si and F cannot be controlled independently of each other, as in the $SiF_4/O_2/Ar$ gas supply system, or because C and F cannot be controlled independently of each other, as in the $SiH_4/O_2/Ar/CF_4$ gas supply system, it is not possible to obtain a dielectric film having not only a low dielectric constant and a satisfactory "resistance to moisture" but also an excellent "resistance to heat". Why this desired dielectric film cannot be obtained will be discussed specifically in the following:

First, carbon has a property of elevating the "resistance to moisture", but if the film contains excess carbon, the "resistance to heat" is deteriorated. For example, if the carbon concentration is 1×10^{22} atoms/cc or more, in the prior art example in which CO_2 is used in place of O_2, for example, in an example formed by using an $SiH_4/CO_2/Ar/CF_4$ gas supply system, the obtained film is not resistant to a heat treatment of 400°C, and the dielectric constant becomes high.

If the above mentioned control was not conducted, since carbon is short in the gas supply system, when a film is formed by using for example the $SiH_4/O_2/Ar/CF_4$ gas supply system which cannot allow to control C and F independently of each other, the fluorine concentration becomes higher than the carbon concentration in the obtained film, with

the result that the obtained film can have only a deteriorated "resistance to moisture".

An object of at least the preferred embodiment of the present invention is to provide a dielectric film having a low dielectric constant and a satisfactory "resistance to moisture".

Another such object is to provide a silicon based dielectric film containing fluorine and carbon, which has a low dielectric constant and a "resistance to moisture" and a "resistance to heat" enough to give reliability.

A further such object is to provide a process for forming a silicon based dielectric film containing fluorine and carbon, which a low dielectric constant and a "resistance to moisture" and a "resistance to heat" enough to give reliability.

Accordingly in a first aspect, the present invention provides a dielectric film formed by a plasma chemical vapour deposition and comprising silicon doped with fluorine in the concentration range of 4.0×10^{21} atoms/cc to 1.0×10^{22} atoms/cc and carbon in the concentration range of 3.0×10^{19} atoms/cc to 1.0×10^{21} atoms/cc.

In a second aspect, the present invention provides a method of forming a dielectric film comprising silicon doped with fluorine and carbon, comprising the step of supplying a material gas comprising a silicon hydride gas, an oxygen gas, a fluorocarbon gas, and a carbon containing gas selected from the group consisting of a carbon oxide gas and a hydrocarbon gas, into a chamber, and generating a plasma in said chamber to activate at least said oxygen gas so as to form by plasma chemical vapour deposition a dielectric film comprising silicon doped with fluorine in the concentration range of 4.0×10^{21} atoms/cc to 1.0×10^{22} atoms/cc, and carbon in the concentration range of 3.0×10^{19} atoms/cc to 1.0×10^{21} atoms/cc on a substrate located in said chamber.

According to a preferred embodiment of this aspect of the present invention, there is provided a process for forming a plasma CVD dielectric film, comprising the step of supplying a material gas composed of a silicon hydride gas, an oxygen gas, a fluorocarbon gas, an argon gas and a carbon oxide gas, into a chamber, and generating a plasma in the chamber to activate the gases, so as to form a plasma CVD dielectric film containing silicon as a basic material, fluorine in the concentration range

of 4.0 x 10^{21} atoms/cc to 1.0 x 10^{22} atoms/cc, and carbon in the concentration range of 3.0 x 10^{19} atoms/cc to 1.0 x 10^{21} atoms/cc, on a semiconductor substrate located in the chamber.

In a third aspect, the present invention provides a method of forming a dielectric film comprising silicon doped with fluorine and carbon, comprising the step of supplying a material gas comprising a silicon fluorine gas, an oxygen gas, and a carbon containing gas selected from the group comprising a carbon oxide gas and a hydrocarbon gas, into a chamber, and generating a plasma in said chamber to activate at least said oxygen gas, so as to form by plasma chemical vapour deposition a dielectric film comprising silicon doped with fluorine in the concentration range of 4.0 x 10^{21} atoms/cc to 1.0 x 10^{22} atoms/cc, and carbon in the concentration range of 3.0 x 10^{19} atoms/cc to 1.0 x 10^{21} atoms/cc on a substrate located in the chamber.

According to a preferred embodiment of this aspect of the present invention, there is provided a process for forming a plasma CVD dielectric film, comprising the step of supplying a material gas composed of a silicon fluorine gas, an oxygen gas, an argon gas and a carbon oxide gas, into a chamber, and generating a plasma in the chamber to activate the gases, so as to form a plasma CVD dielectric film containing silicon as a basic material, fluorine in the concentration range of 4.0 x 10^{21} atoms/cc to 1.0 x 10^{22} atoms/cc and carbon in the concentration range of 3.0 x 10^{19} atoms/cc to 1.0 x 10^{21} atoms/cc, on a semiconductor substrate located in the chamber.

In the above mentioned embodiments, the argon gas can be omitted. In addition, a hydrocarbon gas can be substituted for the carbon oxide gas. Furthermore, it is preferred to control the flow rate of the gas containing the fluorine and the flow rate of the gas containing the carbon, independently of each other.

Specifically, the silicon hydride gas can be one selected from the group consisting of SiH_4, Si_2H_6 (which are generalized by Si_nH_{2n+2}), TEOS, SiH_2Cl_2, or a combination of at least two selected from the same group. The fluorocarbon gas can be one selected from the group consisting of CF_4, C_2F_6, CHF_3, C_4F_8, or a combination of at least two selected from the group. The silicon fluoride gas can be one selected from the group consisting of SiF_4, TEFS (trisethoxyfluorosilane)

and a fluorine containing organic silicon compound, or a combination of at least two selected from the same group.

Alternatively, when the hydrocarbon gas is used in place of the carbon oxide gas, the hydrocarbon gas can be one selected from the group consisting of C_2H_2, CH_4, C_2H_6, C_3H_8. In this case, similarly, the silicon hydride gas can be one selected from the group consisting of SiH_4, Si_2H_6, TEOS, SiH_2Cl_2, or a combination of at least two selected from the same group. The fluorocarbon gas can be one selected from the group consisting CF_4, C_2F_6, CHF_3, C_4F_8, or a combination of at least two selected from the same group. The silicon fluoride gas can be one selected from the group consisting of SiF_4, TEFS and a fluorine containing organic silicon compound, or a combination of at least two selected from the same group.

Furthermore, the silicon hydride gas can be added into the material gas composed of the silicon fluoride gas, the oxygen gas, the argon gas and the carbon oxide gas. In this case, the silicon hydride gas can be one selected from the group consisting SiH_4, Si_2H_6, TEOS, SiH_2Cl_2, or a combination of at least two selected from the same group.

On the other hand, a plasma source for generating the above mentioned plasma is preferred to be a source for generating a high density plasma such as an electron cyclotron resonance plasma, an inductive coupling type plasma, and a helicon plasma.

Preferred features of the present invention will now be described, purely by way of example only, with reference to the accompanying drawings, in which:-

Fig. 1 is a diagrammatic sectional view of a plasma CVD apparatus for illustrating one example of the process for forming the prior art plasma CVD dielectric film;

Fig. 2 is a diagrammatic sectional view of another plasma CVD apparatus for illustrating another example of the process for forming the prior art plasma CVD dielectric film;

Fig. 3 is a graph showing the relation between the fluorine concentration, the carbon concentration and the "resistance to moisture", for illustrating the plasma CVD dielectric film in accordance with the present invention;

Fig. 4 is a diagrammatic sectional view of a plasma CVD apparatus for illustrating a first embodiment of a process for forming a plasma CVD dielectric film; and

Fig. 5 is a diagrammatic sectional view of another plasma CVD apparatus for illustrating a second embodiment of the process for forming a plasma CVD dielectric film.

Description of the Preferred embodiments

Referring to Fig. 3, there is shown a graph showing the relation between the fluorine concentration, the carbon concentration and the "resistance to moisture" of a plasma CVD dielectric film in accordance with the present invention.

The graph of Fig. 3 shows the result of experiments conducted by the inventor, concerning the relation between the fluorine concentration, the carbon concentration and the "resistance to moisture".

As shown in Fig. 3, if the fluorine concentration increases, the "resistance to moisture" was deteriorated. For example, a SiOF film formed to have the fluorine concentration of 1.0×10^{22} atoms/cc showed the Si-OH+O-OH absorption of 27% (arbitrary unit) when it was measured by an FT-IR (Fourier Transform infrared spectroscopy) technique after a PCT (pressure cooker text) was performed for 100 hours. The Si-OH+O-OH absorption is one parameter indicating a moisture absorption property. On the other hand, if the carbon concentration increases, the "resistance to moisture" was improved. For example, in the FT-IR measurement, a SiOF film formed to have the carbon concentration of about 1.0×10^{21} atoms/cc showed the Si-OH+O-OH absorption of 13% (arbitrary unit), which is more excellent than a PE-TEOS (plasma enhanced tetraethoxysilane) film. However, as regards the "resistance to heat", it was confirmed that if the carbon concentration reaches 1.0×10^{21} atoms/cc, the formed SiOF film changes its film quality with the heat treatment of 400°C, so that the dielectric constant becomes high.

From the above mentioned result of the experiments, the inventor reached confidence that if F, C, O and Si in the introduced material gases can be controlled independently of each other, it is possible to obtain a plasma CVD fluorine-doped silicon oxide film having a desired dielectric constant, a high "resistance to moisture" and a desired "resistance to heat". The inventor conducted various experiments of the dielectric constant and the "resistance to moisture", by forming the plasma CVD fluorine-doped silicon oxide film while preparing various combinations of material gases and changing the gas flow rate of respective material gases, for the purpose of determining the fluorine concentration and the

carbon concentration which cause the fluorine-doped silicon oxide film to have excellent dielectric constant, "resistance to moisture" and "resistance to heat". As a result, the inventor found out that, for obtaining the fluorine-doped silicon oxide film having excellent dielectric constant, "resistance to moisture" and "resistance to heat", the fluorine concentration is in the range of 4.0×10^{21} atoms/cc to 1.0×10^{22} atoms/cc, and the carbon concentration is in the range of 3.0×10^{19} atoms/cc to 1.0×10^{21} atoms/cc.

Referring to Fig. 4, there is shown a diagrammatic sectional view of a plasma CVD apparatus for illustrating a first embodiment of a process for forming a plasma CVD dielectric film. For the purpose of obtaining the oxide film having a low desired dielectric constant and a satisfactory "resistance to moisture", the P-SiOF dielectric film was formed by a RF-biased ECR-CVD process using a microwave ECR plasma CVD apparatus shown in Fig. 4.

First, in order to be able to control F, C, O and Si independently of each other, the gas composition was made to $SiH_4/O_2/Ar/CF_4/CO_2$. O_2 is introduced with the flow rate of 75-100 sccm through a first gas nozzle 1 into a plasma chamber 7 surrounded by a magnet coil 5, and on the other hand, SiH_4 of the flow rate of 40-50 sccm, CF_4 of the flow rate of 10-20 sccm, Ar of the flow rate of 0-100 sccm, and CO_2 of the flow rate of 5-10 sccm, are introduced through a second gas nozzle 2 into a reaction chamber 6 in communication with the plasma chamber 7. Microwave of 2.45 GHz and 20 KW is introduced into the plasma chamber 7, so as to activate the gas, and the activated gas is supplied to the reaction chamber 6 by action of a magnetic field generated by the magnet coil 5. A P-SiOF

film is deposited on a wafer 31 held on an electrostatic chuck 3 which is connected to a RF power supply 4 and which is biased with 1.0-1.5 KW.

In the P-SiOF film thus formed, the fluorine concentration is determined by the flow rate of CF_4, or the flow ratio $(O_2+CO_2)/SiH_4$, and the carbon concentration is determined by the flow rate of CO_2+CF_4. Namely, the fluorine concentration and the carbon concentration can be controlled independently of each other. By setting the gas flow rates, the microwave power and the RF power as mentioned above to realize a desired combination of the fluorine concentration and the carbon concentration, the fluorine concentration of 7.0×10^{21} atoms/cc and the carbon concentration of 3.0×10^{20} atoms/cc was obtained in the P-SiOF film.

In the above mentioned gas supplying system, therefore, it could be easily understood that, since the fluorine concentration and the carbon concentration can be controlled independently of each other by controlling the flow rate of the CF_4 gas concerning the fluorine concentration and by controlling the flow rate of the CO_2+CF_4 gas concerning the carbon concentration, it was possible to easily form the P-SiOF film having the fluorine concentration of 7.0×10^{21} atoms/cc and the carbon concentration of 3.0×10^{20} atoms/cc. As a result, there was obtained the plasma CVD F- and C-doped silicon oxide dielectric film having a low dielectric constant of 3.0, and a "resistance to moisture" able to resist the CMP processing.

The wafer having the plasma CVD F- and C-doped silicon oxide dielectric film formed as mentioned above, was introduced into a heat treatment chamber, and an annealing treatment was conducted in an N_2 atmosphere at an annealing temperature of 400°C for ten minutes. The

"resistance to moisture" of the annealed plasma CVD F- and C-doped silicon oxide dielectric film was measured by FT-IR, again. Neither the Si-OH absorption nor the H-OH absorption changed. Furthermore, after the wafer was left for one month, the "resistance to moisture" of the plasma CVD F- and C-doped silicon oxide dielectric film was measured by FT-IR. The Si-OH absorption and the H-OH absorption did not change substantially.

The above mentioned experiment result shows that there was obtained the plasma CVD F- and C-doped silicon oxide dielectric film having the low dielectric constant of 3.0, the "resistance to moisture" able to resist the CMP processing, and a satisfactory "resistance to heat".

Referring to Fig. 5, there is shown a diagrammatic sectional view of another plasma CVD apparatus for illustrating a second embodiment of the process for forming a plasma CVD dielectric film. For the purpose of obtaining the P-SiOF dielectric film having a low dielectric constant and a satisfactory "resistance to moisture", the P-SiOF film was formed by a helicon plasma CVD apparatus shown in Fig. 5, which is one kind of the chemical vapor deposition apparatus.

In order to make it easy to control the gas composition, the gas composition was made to $SiF_4/O_2/Ar/CO_2$. O_2 gas and Ar gas are supplied through a first gas nozzle 8 into a plasma chamber 13 formed of a quartz tube 16 and surrounded by a magnet coil 11 and an antenna 14 connected to a 13.56 MHz RF source 33. SiF_4 gas and CO_2 gas are supplied through a second gas nozzle 9 into a reaction chamber 12. In cooperation of a magnetic field generated by the magnet coil 11 and a helicon wave generated by the antenna 13 driven with the 13.56 MHz RF

source 33, a plasma is generated and the gas is activated. Thus, a P-SiOF film is formed on a wafer 31 held on an electrostatic chuck 10 in the reaction chamber 12.

The fluorine concentration in the P-SiOF film thus formed is determined by the flow rate of the SiF_4 gas or the flow ratio of the SiF_4 gas to other gases O_2 + CO_2. On the other hand, the carbon concentration in the P-SiOF film thus formed is determined by the flow rate of CO_2. Namely, the fluorine concentration and the carbon concentration can be controlled independently of each other. With this gas composition, there could be formed the P-SiOF film having a desired fluorine concentration and a desired carbon concentration, similarly to the first embodiment.

Gas combinations other than the above mentioned gas combinations can be considered. Now, variations including the above mentioned gas combinations will be described. In connection to the second embodiment, first, $SiF_4/O_2/Ar/CO_2$ as mentioned above can be exemplified, and furthermore, SiH_4 can be added into $SiF_4/O_2/Ar/CO_2$. In these two variations, CO_2 can be replaced with CO, or C_2H_2, CH_4, C_2H_6 or C_3H_8, or a combination of at least two selected from the group consisting of C_2H_2, CH_4, C_2H_6 and C_3H_8. In all the variations, Ar can be removed.

In connection to the first embodiment, first, $SiH_4/O_2/Ar/CF_4/CO_2$ as mentioned above can be exemplified, and CO_2 can be replaced with CO, or C_2H_2, CH_4, C_2H_6 or C_3H_8, or a combination of at least two selected from the group consisting of C_2H_2, CH_4, C_2H_6 and C_3H_8. In all the variations, Ar can be removed.

Furthermore, in all the above mentioned variations, SiH_4 can be replaced with TEOS, and CF_4 can be replaced with C_2F_6, C_3F_8, C_4F_8 or

CHF_3. In addition, SiF_4 can be replaced with TEFS, FASi-4 (fluorinated alkylsilanes-4, namely, 1,2 bis [methyldifluorosilyl]ethane) or FASi-6 (fluorinated alkylsilanes-6, namely, 1,2 bis [trifluorosilyl]ethane).

In the above mentioned second embodiment, the Ar gas was introduced into the plasma chamber 13, but the Ar gas can be introduced into the reaction chamber 12. In addition, the CF_4 gas, the COx gas or the CxHy gas can be introduced into either the plasma chamber 13 or the reaction chamber 12. However, introduction to the reaction chamber 12 is more preferable than introduction to the plasma chamber 13, since the introduction to the reaction chamber 12 can prevent contamination of the plasma chamber 13.

On the other hand, as regards the plasma generation source, it is possible to use a parallel plate-electrode CVD process using a single frequency of 13.56 MHz, a parallel plate-electrode CVD process using two frequencies of 13.56 MHz and 400 KHz, a ECR-CVD process using a high density plasma of 2.45 GHz, an ICP-CVD process which is an inductive coupling type plasma, a helicon CVD process, or a 13.56 MHz RF-biased helicon CVD process. However, a high density plasma CVD process such as the ICP-CVD, the ECR-CVD and the helicon CVD is preferable.

A feature of the above process is the selection of material gases which can easily control the fluorine concentration and the carbon concentration independently of each other, setting respective flow rates of the material gases at suitable values which can realize a desired fluorine concentration and a desired carbon concentration, and activating the material gases by plasma to form a P-SiOF film. The P-SiOF dielectric film thus formed

has the desired fluorine concentration and the desired carbon concentration can be obtained. Therefore, the P-SiOF dielectric film having a low dielectric constant, a satisfactory "resistance to moisture", and an excellent "resistance to heat" can be obtained.

If the dielectric film thus formed is used in a semiconductor integrated circuit in a multilevel interconnection structure, a crosstalk between wiring conductors can be prevented, and planarization based on the CMP can be performed with no problem.

The invention has thus been shown and described with reference to the specific embodiments. However, it should be noted that the present invention is in no way limited to the details of the illustrated structures but changes and modifications may be made within the scope of the appended claims.

Each feature disclosed in this specification (which term includes the claims) and/or shown in the drawings may be incorporated in the invention independently of other disclosed and/or illustrated features.

The text of the abstract filed herewith is repeated here as part of the specification.

In a process for forming a plasma CVD fluorine-doped SiO_2 dielectric film, a material gas to be supplied to a plasma CVD apparatus is composed to include not only SiH_4 gas, O_2 gas, CF_4 gas and Ar gas but also CO_2 gas, and the amount of carbon and the amount of fluorine included in the material gas are controlled independently of each other, to form a plasma CVD silicon-based SiO_2 dielectric film doped with fluorine in the concentration range of 4.0×10^{21} atoms/cc to 1.0×10^{22} atoms/cc, and carbon in the concentration range of 3.0×10^{19} atoms/cc to 1.0×10^{21} atoms/cc. Thus, the plasma CVD silicon-based SiO_2 dielectric film having a low dielectric content and a sufficient "resistance to moisture" is obtained.

CLAIMS

1. A dielectric film formed by a plasma chemical vapour deposition and comprising silicon doped with fluorine in the concentration range of 4.0×10^{21} atoms/cc to 1.0×10^{22} atoms/cc and carbon in the concentration range of 3.0×10^{19} atoms/cc to 1.0×10^{21} atoms/cc.

2. A method of forming a dielectric film comprising silicon doped with fluorine and carbon, comprising the step of supplying a material gas comprising a silicon hydride gas, an oxygen gas, a fluorocarbon gas, and a carbon containing gas selected from the group consisting of a carbon oxide gas and a hydrocarbon gas, into a chamber, and generating a plasma in said chamber to activate at least said oxygen gas so as to form by plasma chemical vapour deposition a dielectric film comprising silicon doped with fluorine in the concentration range of 4.0×10^{21} atoms/cc to 1.0×10^{22} atoms/cc, and carbon in the concentration range of 3.0×10^{19} atoms/cc to 1.0×10^{21} atoms/cc on a substrate located in said chamber.

3. A method according to Claim 2 wherein said material gas further comprises an argon gas.

4. A method according to Claim 2 or 3, wherein the flow rate of said fluorocarbon gas and the flow rate of said carbon containing gas are controlled independently of each other.

5. A method according to any of Claims 2 to 4, wherein said silicon hydride gas comprises one of the group comprising of SiH_4, Si_2H_6, TEOS and SiH_2Cl_2 or a combination of at least two selected from the same group, and said fluorocarbon gas comprises one of the group consisting of CF_4, C_2F_6, CHF_3, C_3F_8, or a combination of at least two selected from the same group.

6. A method according to Claim 5 wherein said hydrocarbon gas comprises one of the group consisting of C_2H_2, CH_4, C_2H_6 and C_3H_8 or a combination of at least two selected from the same group.

7. A method of forming a dielectric film comprising silicon doped with fluorine and carbon, comprising the step of supplying a material gas comprising a silicon fluorine gas, an oxygen gas, and a carbon containing gas selected from the group comprising a carbon oxide gas and a hydrocarbon gas, into a chamber, and generating a plasma in said chamber to activate at least said oxygen gas, so as to form by plasma chemical vapour deposition a dielectric film comprising silicon doped with fluorine in the concentration range of 4.0 x 10^{21} atoms/cc to 1.0 x 10^{22} atoms/cc, and carbon in the concentration range of 3.0 x 10^{19} atoms/cc to 1.0 x 10^{21} atoms/cc on a substrate located in the chamber.

8. A method according to Claim 7, wherein said material gas further comprises an argon gas.

9. A method according to Claim 7 or 8, wherein the flow rate of said silicon fluoride gas and the flow rate of said carbon containing gas are controlled independently of each other.

10. A method according to any of Claims 7 to 9, wherein said silicon gas comprises one of the group consisting of SiF_4, TEFS and a fluorine containing organic silicon compound, or a combination of at least two selected from the same group.

11. A method according to any of Claims 7 to 10, wherein said material gas further comprises a silicon hydride gas.

12. A method according to Claim 11 wherein said silicon fluoride gas comprises one of the group consisting of SiF_4, TEOS and a fluorine containing organic silicon compound, or a combination of at least two selected from the same group, and said silicon hydride gas comprises one of the group consisting of SiH_4, Si_2H_6, TEOS and SiH_2Cl_2 or a combination of at least two selected from the same group.

13. A method according to Claim 12, wherein said hydrocarbon gas comprises one of the group consisting of C_2H_2, CH_4, C_2H_6 and C_3H_8 or a combination of at least two selected from the same group.

14. A method according to any of Claims 2 to 13, wherein said plasma is a high density plasma comprising one of the group consisting of an electron cyclotron resonance plasma, an inductive coupling type plasma and a helicon plasma.

15. A method according to Claim 14, wherein a high frequency bias is applied to said substrate on which said plasma CVD silicon oxide dielectric film is to be formed.

16. A dielectric film substantially as herein described with reference to Figures 3 to 5 of the accompanying drawings.

17. A method of forming a dielectric film substantially as herein described with reference to Figures 3 to 5 of the accompanying drawings.

The Patent Office

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Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): H1K(KJACX,KJAX); C7F(FHB)

Int Cl (Ed.6): H01L

Other: ON LINE,W.P.I.

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
A	EP 0599730 A2	SUMITOMO	
A	US 5571578	TOSHIBA	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
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